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(56) Documents cited
GB 1552538 A GB 1309871 A GB 1214848 A
GB 1149081 A GB 0856628 A

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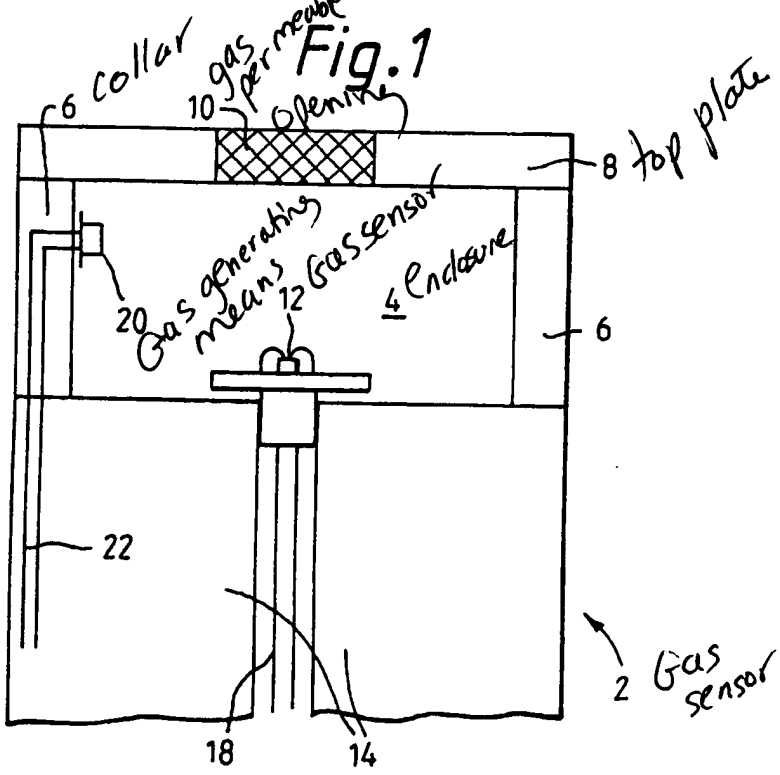
# (54) Gas sensor and calibration device

(57) A gas sensor device (2) comprises an enclosure (4) within which is housed both a gas sensor (12) and electrochemical calibrant gas generating means (20). The means (20) may be remotely electrically operated and is comprised such that minimal attention thereto is required during the lifetime of the device (2). The gas sensor (12) may be a metal oxide semiconductor device for sensing hydrogen, in which case means (2), in the form of a pair of electrodes and bridging electrolyte, generates hydrogen. Alternatively if carbon monoxide is to be sensed sensor (12) is an electrochemical sensor and may comprise a pair of platinum electrodes sandwiching an electrolyte.

Fig.1

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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

Fig.1

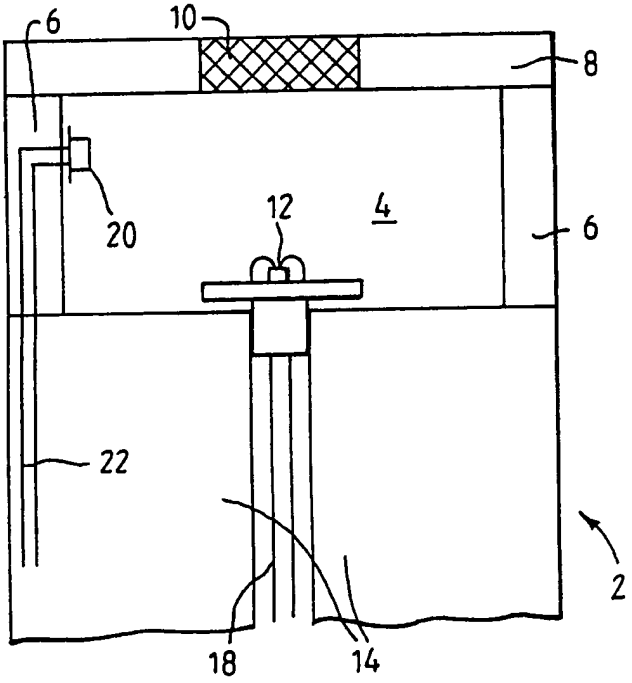



Fig.3

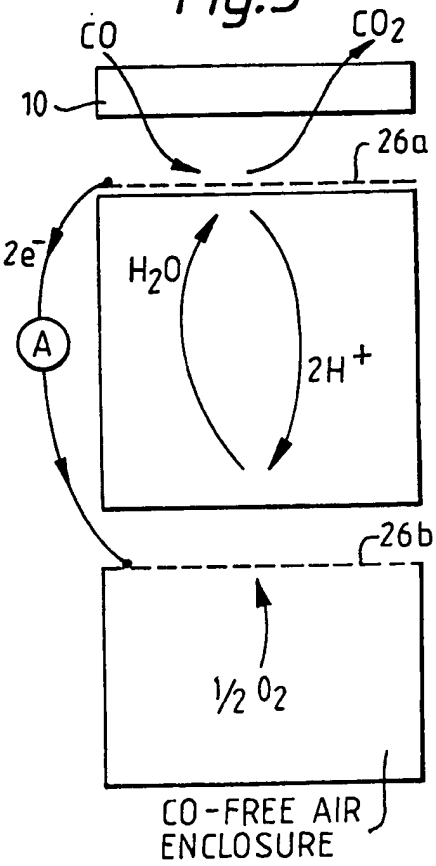
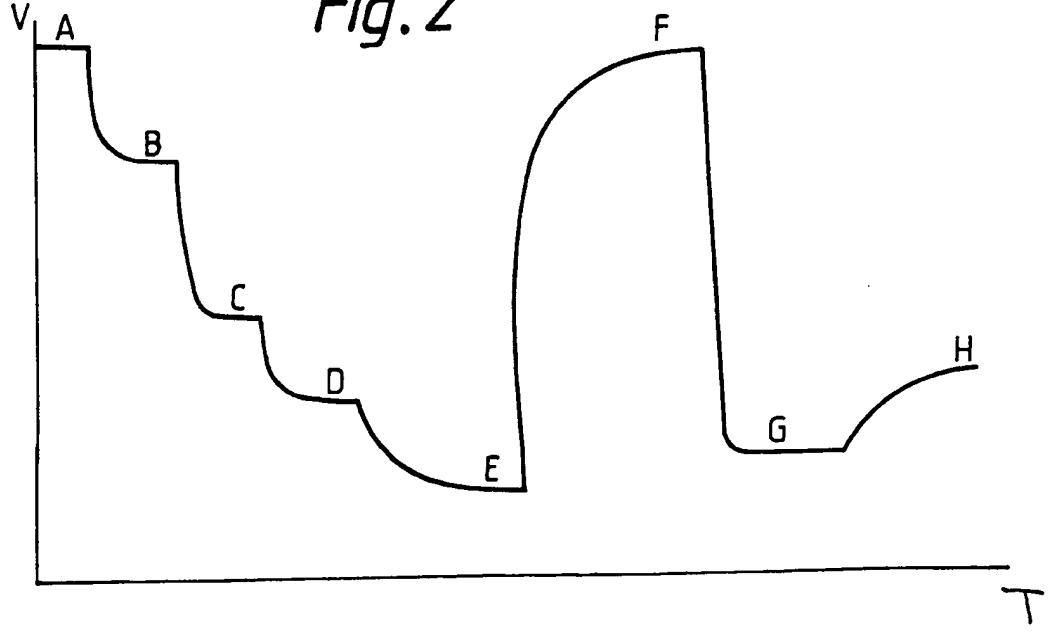



Fig.2



# GAS SENSOR DEVICE

The present invention relates to gas sensor devices and has particular, though not exclusive, relevance to such devices as are used, for example, in detecting gases produced during the burning of materials.

Gas sensor devices are well known as being capable of detecting small concentrations (0-several thousand ppm) of specific gases present in ambient conditions. All such devices require calibrating before use in order to standardise their response both to the gas they are to detect and to ambient conditions which they must ignore. Such calibrations require very low concentrations of the specific gas to which the devices are sensitive. Obtaining the specific gas to be detected in such a low concentration is, in itself, a difficult task to achieve, and generally this is done by way of a pre-filled cylinder containing the specific gas in air at the required concentration. Such cylinders tend to be expensive and must be replaced when empty in order to continue operating the sensor device accurately. An example of such a sensor device requiring calibration via a cylinder is that disclosed in Soviet Union patent application publication number SU 1429147A. This patent application describes a system incorporating a gas sensor which must be "zeroed" by admitting inert gas into the sensor chamber by way of a cylinder. The cylinder is arranged to contain gas at a predetermined temperature in order for the correct zeroing of the gas sensor.

Furthermore, as gas sensor devices are practically remote stations often positioned in unobtrusive out-of-the-way places, applying the calibrant gas via a cylinder as detailed above, may become a somewhat arduous task.

It is thus an object of the present invention to provide a gas sensor device wherein the above problems are at least alleviated.

According to the present invention there is provided a gas sensor device comprising: a gas sensor and an electrochemical gas generating means for the electrochemical generation of gas for calibration of the gas sensor. Thus, the need for a separate remote supply of calibrant gas is obviated. Furthermore, as the gas generating means is electrochemical, it is capable of operation only as and when required by the supply of a controllable electric current.

Advantageously, both the gas sensor and the electrochemical gas generating means are housed within an enclosure having an opening permeable only to gas.

Preferably, the electrochemical gas generating means comprises a pair of electrically conductive, metallic electrodes and a bridging electrolyte.

In use of the device, the electrochemical gas generating means may be arranged to produce calibrant gas only sporadically.

Preferably, the gas sensor is sensitive primarily to carbon monoxide.

Additionally or alternatively, the gas sensor is sensitive to hydrogen.

Preferably, the calibrant gas is hydrogen.

The invention will now be described, by way of examples only, with reference to the following drawings of which:

Figure 1 illustrates schematically a metal oxide semiconductor gas sensor device in accordance with the present invention;

Figure 2 shows the variation in output voltage with time on exposure of the device to various concentrations of the gas to be sensed, and

Figure 3 illustrates schematically an electrochemical gas sensor for inclusion with the present invention;

Figure 1 illustrates a first embodiment of the present invention. The gas sensor device is shown generally as 2. The device comprises an enclosure 4 which is formed from a collar 6 above and on which is mounted a top plat 8. In the centre of

the top plate 8 there is formed a gas-permeable opening 10 in the form of a sintered stainless steel disc. The enclosure 4 is impervious to fluid except for the gas-permeable opening 10.

Housed centrally within the enclosure 4 is a metal oxide semiconductor (MOS) gas sensor 12. The operation of such a sensor is well known in the art and so will not be described herein. The sensor 12 is mounted on a supporting member 14 having a central channel 18 through which electrical connections 22 run between the MOS sensor 12 to a controller device (not shown). Also housed within the enclosure 4 and mounted on collar 6 is an electrochemical gas generating means 20. The gas generator 20 comprises a pair of metal electrodes and a bridging electrolyte (not shown) and has electrical connections 22 to the controller device (not shown) through supporting member 14.

The electrochemical gas generator means 20 is required to sporadically produce a gas for calibration of the MOS sensor 12. This is achieved as follows: when a current is passed through electrical connections 22, electrolysis of the bridging electrolyte occurs at the metal electrodes. The electrodes are chosen to be preferentially formed from noble metals and the electrolyte is chosen depending on which gas is to be used as the calibrant gas.

In the embodiment of Figure 1, the sensor 12 was chosen to be a MOS hydrogen sensor and the calibrant gas required was also hydrogen. The electrodes of the electrochemical generator means 20 were gold and the electrolyte phosphoros pentoxide. This particular electrolyte was chosen as, because it is hydroscopic and gains water from absorbing atmospheric moisture, the gas generator 20 will not dry out and hence has, theoretically, an infinite lifetime.

On passing an electric current through gas generator 20 via connections 22, only water is electrolysed, thus causing hydrogen and oxygen to be produced at the gold electrodes; the reaction being

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}.$$

The internal volume of enclosure 4 is approximately 1.25ml,

and assuming that none of the generated hydrogen gas may escape from the enclosure, then the concentration of calibrant hydrogen gas generated by gas generator 20 within the enclosure 4 (the enclosure having a volume of approximately 2.5cm$^3$) will be dependent upon the current passed through the gas generator 20, according to the relationship: 0.1mAs=10ppm

where mA = milliamps
s = seconds for which the current is passed
ppm = parts per million, this relationship being dependent on the gas being generated, all volume, temperature pressure etc.

Thus the concentration of calibrant gas generated by gas generator 20 may be controlled by controlling the amplitude and duration of the current passed to the metal electrodes.

Referring now to Figure 2, experimental results obtained by using the device of Figure 1 are detailed. The abscissa represents the time (in minutes) over which the experiment was run; and the ordinate represents the output (in mV) of the sensor 12.

Once the device 2 is switched on, it requires several minutes during which to stabilise. This stabilisation is reached at point [A] in Figure 2. At this point [2], the gas generator 20 was activated and a current of 20μA was passed continually therethrough for 4 minutes. It will be seen that point [B] was approached asymtotically as a result of the generated hydrogen calibrant gas. Consequently, the current was increased to 40μA and passed through means 20 for a further 4 minutes. It will be seen that point [C] was approached asymtotically as a result of the presence of further generated hydrogen calibrant gas. Consequently also, the current was increased to 60μA and passed through means 20 for a further 4 minutes, and point [D] was approached asymtotically. Finally, the current through means 20 was increased to 80μA for 4 minutes, and stabilisation point [E] was approached asymtotically. This series of events calibrated the sensor 12, as known concentrations of hydrogen gas within enclosur 4 were being generated, in accordance with the above relationship.

Aft r the calibration sequence was completed, the device 2 was allowed t stand in ambient air for a period of 10 minutes,

stabilising at point [F]. Then the ambient air was contaminated with 9.4 ppm hydrogen and subsequently 4.7 ppm hydrogen and the results of the output of device 2 are shown as points [G] and [H] respectively.

Thus, by reference to point [F] and comparison therewith to points [G] and [H]; it is seen that the present invention provides for the quick and efficient calibration of a gas sensor enabling very small (tens of ppm) concentrations of contaminant gas to be subsequently detected.

Referring now also to Figure 3 in which is illustrated an electrochemical gas sensor 24. Such a sensor may replace the MOS gas sensor 12 detailed in Figure 1, yet the remainder of the description of Figure 1 remains valid. Such an electrochemical sensor 24 may be required as an alternative to a MOS sensor 12 in such cases where a different contaminant gas is to be sensed. For example, in the field of fire detection, it is known that for numerous types of fires, an initial smouldering stage occurs during which little smoke or heat is generated, yet gaseous products are evolved. One such product is carbon monoxide (CO), and the MOS sensor 12 is inappropriate for detection of this gas. The electrochemical sensor 24, on the other hand, may be used. However, the electrochemical sensor 24 is also necessarily to be calibrated before accurate use and so falls prey to similar shortcomings as the prior art devices.

The electrochemical sensor 24 shown in Figure 3 comprises two catalytic electrodes 26a, 26b, preferably chosen to be formed from platinum, and which, respectively, form an anode and cathode for the sensor 24. The electrodes 26a, 26b sandwich, and contact a proton (or hydroxyl) conducting electrolyte. Sulphuric acid was chosen as the electrolyte due to its capability to generate a current from oxidation of carbon monoxide at the electrode 26a. This reation is accompanied by a reduction of protons and oxygen at the enclosed electrode 26b.

The reactions involved when sensor 24 is exposed to carbon monoxide are as follows:

at anode 26a: $CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$,

at cathode 26b: $2H^+ 2e^- \rightarrow H_{2(g)}$

or at cathode 26b: $1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O_{(1)}$

The sensor 24 exhibits a cross-sensitivity to hydrogen gas, and may sense such gas in a similar manner to the sensing of carbon monoxide as herebefore described. Thus, the device 2 incorporating sensor 24 may be calibrated by electrochemical gas generator means 20, because generator 20 is configured to produce hydrogen gas.

Although sensor 24 exhibits a cross-sensitivity to hydrogen gas as well as being sensitive to carbon monoxide gas; it is not as sensitive to hydrogen as to carbon monoxide. Thus, by setting the sensitivity of sensor 24 to an appropriate level (which may easily be achieved by the controller device), calibration of sensor 24 may be achieved by generator 20 generating hydrogen without causing the sensor 24 to activate an alarm because of a false assumption of sensing carbon monoxide gas.

Alternatively, the cross-sensitivity of sensor 24 may be utilised to generate a response to hydrogen gas produced by means 20 without triggering an alarm which would be produced by the presence of carbon monoxide gas; in this way, the sensor 24 may be verified as functioning correctly without triggering an alarm.

It will be appreciated by those skilled in the art that various gases may be generated by electrochemical gas generator 20 in order to be used as calibrants. This would entail only the alteration of the electrodes and electrolyte. Alternative suitable electrodes for the production of hydrogen include platinum, silver, or consumable electrodes such as copper or zinc. Alternatively, graphite and polysilicon have been found to be effective. Suitable electrolytes include a hydrogel (for example polyHEMA or PVA), a doped hydrogel, or a deliquescent material such as calcium chloride. It will be understood that alternative electrolytes may produce alternative calibrant gases dependent upon those utilised. Alternative calibrant gases may be required when an alternative gas sensor, other than those

described herebefore, are employed.

It will be understood that the gas sensor 12,24 need not necessarily be housed in the same enclosure 4 as the electrochemical gas generator 20. They may equally well be housed in separate enclosures connected by a conduit or the like.

Thus the invention described above provides for an efficient gas sensor device, wherein the means for providing calibrant gas is housed within the device and requires minimal interference during the lifetime of the device.

CLAIMS

1. A gas sensor device comprising : a gas sensor and an electrochemical gas generating means for the electrochemical generation of gas for calibration of the gas sensor.
2. A gas sensor device according to claim 1 wherein both the gas sensor and the electrochemical gas generating means are housed within an enclosure having an opening permeable only by gas.
3. A gas sensor device according to claim 1 or 2 wherein the electrochemical gas generating means comprises a pair of electrically conductive, metallic electrodes and a bridging electrolyte.
4. A gas sensor device according to any one of claims 1-3 wherein the electrochemical gas generating means is arranged for sporadic production of gas for calibration.
5. A gas sensor device according to any one of the preceding claims wherein the electrochemical gas generating means is effective to produce hydrogen.
6. A gas sensor device according to any one of the preceding claims wherein the gas sensor is a metal oxide semiconductor device.
7. A gas sensor device according to Claim 6 wherein the metal oxide semiconductor device is effective to sense hydrogen.
8. A gas sensor device according to any one of Claims 1-5 wherein the gas sensor is an electrochemical gas sensor.
9. A gas sensor device according to Claim 8 wherein the electrochemical gas sensor is effective to sense carbon monoxide.
10. A gas sensor device as substantially herein described with reference to the accompanying drawings.

**Patents Act 1977**
**Examiner's report to the Comptroller under Section 17 (The Search Report)**

Application number
9107686.9

**Relevant Technical fields**

(i) UK Cl (Edition K ) G1A (AFB,ADJ); G1N (NAHA,NBKT, NBMX,NBPM,NBPX,NCGA,NCGB,NCGC, NCGD,NCGE,NCGF,NCGG)

(ii) Int CL (Edition 5 ) G01N

Search Examiner
H COLLINGHAM

**Databases** (see over)

(i) UK Patent Office

(ii)

Date of Search
24 MAY 1991

Documents considered relevant following a search in respect of claims 1 TO 10

| Category (see over) | Identity of document and relevant passages | Relevant to claim(s) |
|---|---|---|
| X | GB 1552538 A (BAYER) whole document | 1,3,4,8,9 |
| X | GB 1309871 A (NORTH HANTS) whole document | 1,3,4,8 |
| X | GB 1214848 A (KENT) whole document | 1,2,4,8 |
| X | GB 1149081 A (NRDC) whole document | 1,2,3,4,8 |
| X | GB 0856628 A (U.K.A.E.A.) whole document | 1,3,4,5,8 |

| Category | Identity of document and relevant passages | Relevant to claim(s) |
|---|---|---|
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